



Europäisches Patentamt
European Patent Office
Office européen des brevets

Publication number:

**0 399 706
A2**

EUROPEAN PATENT APPLICATION

Application number: 90305117.5

Int. Cl.⁵: **D06M 15/643**

Date of filing: 11.05.90

Priority: 24.05.89 GB 8911970

Date of publication of application:
28.11.90 Bulletin 90/48

Designated Contracting States:
BE DE ES FR GB IT NL

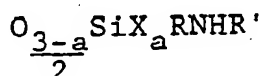
Applicant: **Dow Corning Limited**
Inveresk House 1 Aldywch
London WC2R 0HF(GB)

Inventor: **Cray, Stephen Edward**
10 Doniford Close Sully
South Glamorgan Wales(GB)
Inventor: **Renauld, Franck André Daniel**
Schransdreef 49
B-1900 Overijse(BE)

Representative: **Vandamme, Luc Johan Roger**
et al
Dow Corning Limited Cardiff Road
Barry South Glamorgan CF6 7YL Wales(GB)

Method of treating fibrous materials.

A method of treating fibrous materials comprises applying a composition comprising as sole amine containing organosilicon compound the reaction product of an organopolysiloxane having



groups with one or more monoepoxides. X denotes a monovalent C₁₋₈ hydrocarbon group, R is an alkylene group, R' is H or a group of the formula RZ, Z being NHX, NH₂, NHRNH₂ or NHRNHX. No more than 10% of all amine groups may be primary amine groups. The composition is preferably applied as an emulsion. Fibres thus treated are soft and show less yellowing than the prior art.

EP 0 399 706 A2

METHOD OF TREATING FIBROUS MATERIALS

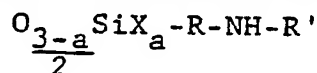
This invention relates to a method of treating fibrous materials and more specifically to a method of treating textile materials.

With the expression fibrous materials is meant fibres of synthetic or naturally occurring materials, for example wool, cotton, polyester, carbon and blends of these. The invention relates to the treatment of the fibres as such as well as to the treatment of fabrics or textiles incorporating the fibres.

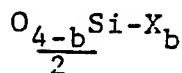
It is known to treat fibrous materials with compositions comprising amine-containing silicon compounds for imparting desirable properties, e.g. softness, water repellency, lubricity and crease resistance thereto. G.B. patent specification 1 491 747 for example provides a composition for treatment of synthetic fibres which comprises 1 part of certain aminosilanes and 1 to 20 parts of certain epoxysiloxanes. G.B. patent specification 1 296 136 provides a process for the treatment of synthetic organic textile fibres which includes the treatment with a composition comprising either a) a mixture of an aminosiloxane and a polyepoxide, b) a mixture of a liquid epoxysiloxane and a polyamine or c) a mixture of a liquid epoxysiloxane and an aminosiloxane. However, these materials tend to give a certain amount of yellowing of the treated fibres. In U.S. patent 4 757 121 it is proposed to overcome the yellowing problem when treating synthetic fibre made waddings by using a composition comprising 100 parts by weight of a combination of two organopolysiloxanes composed of from 5 to 95% by weight of an amino-substituted organopolysiloxane, and 95 to 5% by weight of a second amino-substituted organopolysiloxane, which is a reaction product of a liquid amino-substituted organopolysiloxane and a liquid organic epoxy compound, from 1 to 50 parts by weight of an epoxy-containing alkoxy silane and from 1 to 50 parts by weight of a monoepoxy compound.

We have found that an improved treating composition can be made by restricting the amine-containing organosiloxane to those which are prereacted with a monoepoxide.

According to the invention there is provided a method of treating fibrous materials, which comprises the application to fibrous materials of a composition comprising as sole amine-containing organosilicon compound the reaction product of an organopolysiloxane having at least one unit of the general formula

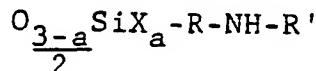


and at least one unit having the general formula

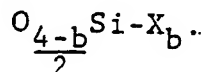


with one or more monoepoxides, wherein X denotes a monovalent hydrocarbon having up to 8 carbon atoms, R denotes a divalent alkylene group, R' denotes a hydrogen atom or a group of the formula R-Z, wherein Z is NHX, NH₂, NHRNH₂ or NHRNHX, a has a value of 1 or 2 and b has a value of 2 or 3.

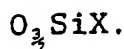
The organopolysiloxane used in the preparation of the reaction product may be any siloxane polymer having at least 1 unit of the general formula



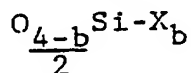
and at least one unit having the general formula



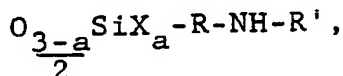
Preferably it is a substantially linear polydiorganosiloxane polymer, although small amounts of units which cause branching of the siloxane are possible. Such units, which should not be present in more than 5% of the total number of units, have the general structure



The substituent X may be any hydrocarbon group having up to 8 carbon atoms, for example alkyl, aryl, alkenyl, alkylaryl and arylalkyl. Preferably X denotes a lower alkyl group. Preferably at least 80% and most preferably substantially all X groups are methyl groups. It is, however, possible that small amounts of other substituents are present on silicon atoms, for example hydroxyl or alkoxy groups. The group R is a divalent alkylene group, preferably having up to 8 carbon atoms, most preferably from 3 to 8 carbon atoms. Examples of the R group include dimethylene, propylene, isobutylene and hexylene. The groups R' may be hydrogen or a group of the formula RZ, wherein Z denotes a primary or secondary amine group or a diamine of the formula NHRNH₂ or NHRNHX. a has a value of 1 or 2, which means that the unit may be located in the siloxane chain or may be an end-unit of the siloxane chain. Examples of the amine-containing substituent are OSi(CH₃)(CH₂)₃NH₂, OSi(CH₃)CH₂CH(CH₃)CH₂NH₂, OSi(CH₃)CH₂CH(CH₃)CH₂NH(CH₂)₂NH₂, O₂Si(CH₃)₂CH₂CH(CH₃)CH₂NH(CH₂CH₃), O₂Si(CH₃)₂(CH₂)₃NH(CH₂)₃NH(CH₂)₃NH₂. The other units of the organopolysiloxane are units of the general formula

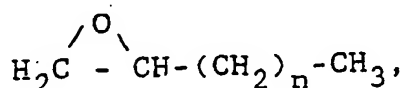


wherein b has a value of 2 or 3 and X has the meaning as above. This means that the units may be present in the siloxane chain or as endgroups of the chain. It is preferred that polydiorganosiloxane having from 10 to 1000 siloxane units, particularly from 100 to 500 units, most preferably about 400 units are used. The viscosity of the polydiorganosiloxane tends to determine the softness which is imparted to the treated materials, the higher the viscosity, the softer the finish. However, for reasons of practicality it is preferred to use those materials which are liquid at room temperature. It is also preferred that from 0.1 to 20 mole% of all siloxane units are units of the formula



preferably from 1 to 10%, most preferably from 1 to 4%. A particularly advantageous amount is 2%. Amounts above 10% are unlikely to contribute additional beneficial effects to the treated materials. Suitable organopolysiloxanes for the preparation of the reaction product for use in the method of the invention are known in the art and many are commercially available. They can be made by methods known in the art, for example by the condensation of aminofunctional silanes or hydrolysis products thereof with cyclic siloxanes in the presence of endblocking units, for example those provided by hexamethyldisiloxanes.

Monoepoxides employed in the preparation of the reaction product are organic compounds having one epoxy group. By the term epoxy is meant a group composed of oxirane oxygen attached to two vicinal carbon atoms. Monoepoxides which are suitable for use in the present invention are those wherein the substituent of the said vicinal carbon atoms are hydrogen, hydrocarbon groups or ether or ester containing hydrocarbon groups. Preferably one of the carbon atoms has only hydrogen atoms while the other carbon atom has an alkyl group attached to it, which may range from methyl to a linear C₂₁ alkyl group. Most preferred are those monoepoxides wherein the alkyl group has from 1 to 10 carbon atoms, especially from 1 to 4 carbon atoms. Examples of suitable monoepoxides are ethylene oxide, propylene oxide, butadiene monoxide, 2,3-epoxy-cyclopentane, substituted olefin oxides, e.g. 2, 3-epoxy-propylbenzene, epoxy alcohols, e.g. glycidol, 2,3-epoxy-cyclopentanol, 3,4-epoxy-6-methylcyclohexylmethane, glycidyl ethers, e.g. phenyl glycidyl ether, butyl glycidyl ether or glycidyl esters, e.g. glycidyl acetate. Preferred are those monoepoxides of the general formula



wherein n has a value of from 0 to 20, preferably 0 to 8, most preferably 0 to 3.

The reaction product for use in the method of the invention may be prepared according to known

methods. For example, the two reagents may be reacted together in the presence of a low molecular weight aliphatic alcohol or in the presence of a catalytic amount of water. The reaction can be carried out at room temperature in the presence of such catalyst but is preferably carried out at increased temperatures, for example temperatures of 50°C or more. In order to make the reaction more easily handled it may be carried out in the presence of a solvent, which may be the alcohol mentioned above or other suitable solvents. The amount of monoepoxide used in the reaction should be such that no more than 10% of all amine groups in the organopolysiloxane are retained unreacted in the reaction product. Where a primary amine group was present in the organopolysiloxane two monoepoxide molecules can react with the amine. It is preferred that the majority of the amino groups in the reaction product are tertiary amine groups, although the presence of secondary amine groups to the exclusion of tertiary amine groups is also acceptable. The amine groups in the reaction product may thus be tertiary, secondary, a mixture of these, or a mixture of either or both with up to a maximum of 10% primary amine groups.

It is important that the reaction product is used in the method of the invention, and not a mere mixture of the polydiorganosiloxane and the monoepoxide. Mere mixtures which contain polydiorganosiloxanes having relatively high amounts of primary amine groups are not satisfactory, since they will still display a yellowing of the treated materials. Even a mixture of the two components in the presence of water, e.g. by using an emulsion, is unsatisfactory as the yellowing upon treatment with such mixtures or emulsions is worse than treatment according to the invention. Preferably no primary amines are retained in the reaction product. Most preferably no secondary amines are present either in the reaction product.

The method of the invention comprises the application to fibrous materials of a composition comprising as sole amine-containing compound the reaction product as described above. This application may be done in any convenient way. Application methods which are suitable include padding, dipping and spraying of a composition comprising the reaction product. The compositions used may be in any suitable form, e.g. solutions, dispersions or emulsions. The dispersions may be in aqueous or solvent based materials while the emulsions are preferably oil-in-water type emulsions. Especially preferred are emulsions, particularly microemulsions according to European patent specification 138 192. Compositions which are useful in the method of the invention may comprise other ingredients which are useful in treatment compositions for fibrous materials, e.g. fatty acid softeners. Other ingredients e.g. surfactants in the emulsions are also useful. It is, however, preferred that the composition comprises no amine-containing compounds other than the reaction product.

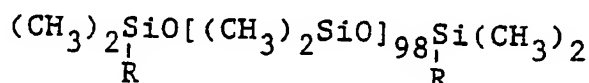
The method of the invention is suitable for the treatment of both naturally occurring and synthetic fibres, for example carbon fibres, polyester fibres, cotton fibres and blends of cotton and polyester fibres. The application may be done at the stage of making the fibres, at the stage of producing the fabrics or in a special treating step later, for example during laundering of a textile fabric. Application may be followed by drying at room temperature or at increased temperatures. After the drying stage a further heat treatment of the fibrous materials is preferred. The latter is particularly useful when the textile fabrics are treated at the time of their production. The presence of small amounts of primary amine groups on the reaction product will increase the durability of the finish on the fibrous materials, especially when they are subjected to laundering operations. Fibrous materials and textiles which are treated according to the method of the invention have an improved softener and lubricity, a pleasant feel and handle, without suffering from yellowing due to the treatment.

In a further aspect of the invention there is provided a fibrous material treated according to the method of the invention. Also included are fabrics or textiles incorporating fibres when treated according to the method of the invention.

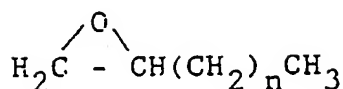
There now follow a number of examples illustrating the invention in which all parts are expressed by weight unless otherwise mentioned.

Examples 1 - 5

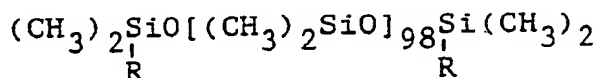
1 molar part of a polydiorganosiloxane compound of the average formula



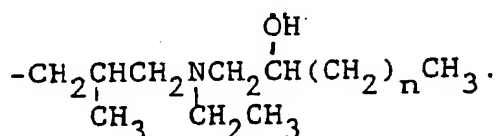
wherein R denotes $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NHCH}_2\text{CH}_3$, was reacted with 2 molar parts of a monoepoxide having the average formula



wherein n was 0, 1, 3, 7 and 9 respectively for Examples 1, 2, 3, 4 and 5 in the presence a mixture of 95 parts of methanol, 3 parts of isopropanol and 2 parts of water at a temperature of 50°C. This yielded a reaction product which is believed to have the average formula



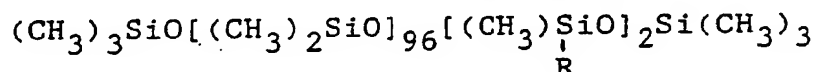
wherein R' denotes



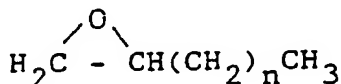
A bath was prepared with a 2.77% solution in perchloro ethylene of the reaction product prepared in Examples 1 to 5 in which a piece of polyester cotton (65/35) was treated by padding. The piece was heated to 110°C for 1 minute, followed by 2 minutes at 180°C after treatment. The piece had picked up 0.5% by weight of the reaction product.

Examples 6 - 10

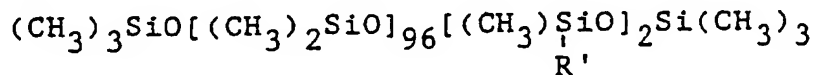
1 molar part of a polydiorganosiloxane compound of the average formula



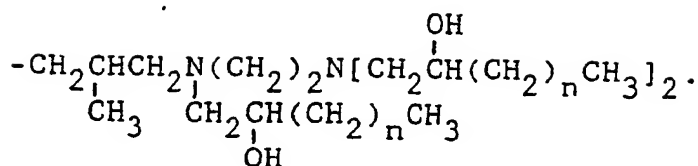
wherein R denotes $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, was reacted with 6 molar parts of a monoepoxide having the average formula



wherein n was 0, 1, 3, 7 and 9 respectively for Examples 6, 7, 8, 9 and 10 in the presence a mixture of 95 parts of methanol, 3 parts of isopropanol and 2 parts of water at a temperature of 50°C. This yielded a reaction product which is believed to have the average formula



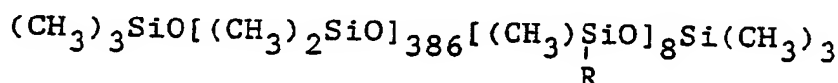
wherein R' denotes



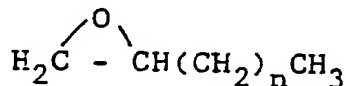
A bath was prepared with a 2.77% solution in perchloro ethylene of the reaction product prepared in Examples 6 to 10, in which a piece of polyester cotton (65/35) was treated by padding. The piece was heated to 110°C for 1 minute, followed by 2 minutes at 180°C after treatment. The piece had picked up 0.5% by weight of the reaction product.

Examples 11 - 15

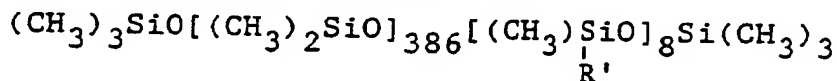
1 molar part of a polydiorganosiloxane compound of the average formula



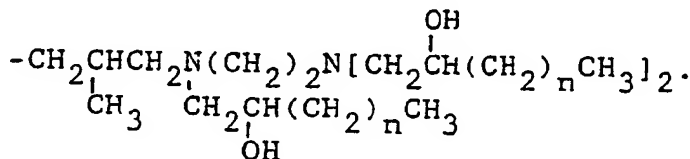
wherein R denotes $-\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$, was reacted with 24 molar parts of a monoepoxide having the average formula



wherein n was 0, 1, 3, 7 and 9 respectively for Examples 11, 12, 13, 14 and 15 in the presence of a mixture of 95 parts of methanol, 3 parts of isopropanol and 2 parts of water at a temperature of 50°C. This yielded a reaction product which is believed to have the average formula



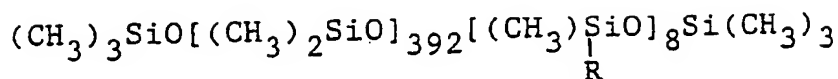
wherein R' denotes



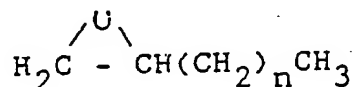
A bath was prepared with a 2.77% solution in perchloro ethylene of the reaction product prepared in Examples 11 to 15, in which a piece of polyester cotton (65/35) was treated by padding. The piece was heated to 110°C for 1 minute, followed by 2 minutes at 180°C after treatment. The piece had picked up 0.5% by weight of the reaction product.

Examples 16 - 20

1 molar part of a polydiorganosiloxane compound of the average formula



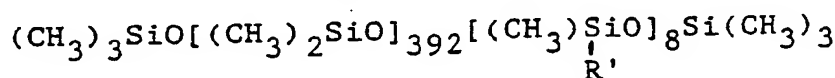
5 wherein R denotes $-(\text{CH}_2)_3\text{NHCH}_2\text{CH}_2\text{NH}_2$, was reacted with 24 molar parts of a monoepoxide having the average formula



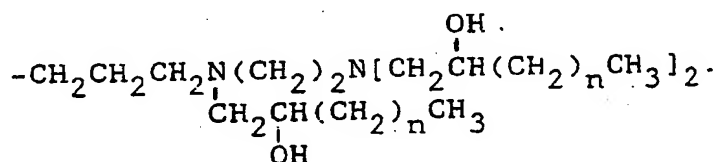
10

wherein n was 0, 1, 3, 7 and 9 respectively for Examples 16, 17, 18, 19 and 20 in the presence of a mixture of 95 parts of methanol, 3 parts of isopropanol and 2 parts of water at a temperature of 50°C . This yielded a reaction product which is believed to have the average formula

15



20 wherein R' denotes

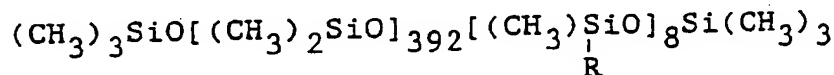


25

30 A bath was prepared with a 2.77% solution in perchloro ethylene of the reaction product prepared in Examples 16 to 20, in which a piece of polyester cotton (65/35) was treated by padding. The piece was heated to 110°C for 1 minute, followed by heating at 180°C for 2 minutes after treatment. The piece had picked up 0.5% by weight of the reaction product.

35 Examples 21 - 22

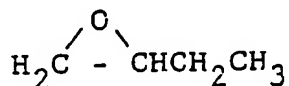
1 molar part of a polydiorganosiloxane compound of the average formula



40

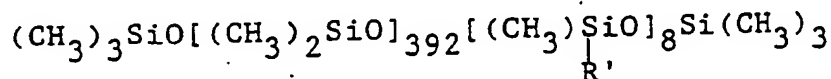
wherein R denotes $-(\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2)\text{NHCH}_2\text{CH}_2\text{NH}_2$, was reacted with 24 molar parts of a monoepoxide having the formula

45



50

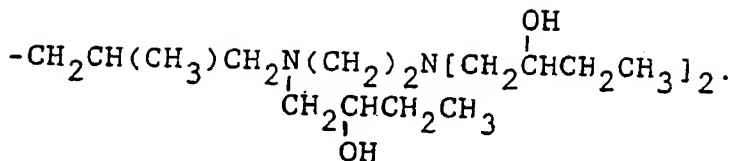
in the presence of a mixture of 95 parts of methanol, 3 parts of isopropanol and 2 parts of water at a temperature of 50°C . This yielded a reaction product which is believed to have the average formula



55

wherein R'

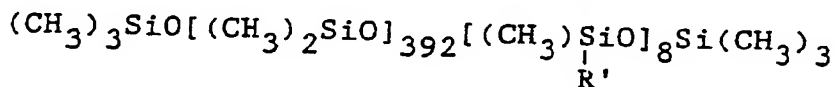
denotes



10 A bath was prepared with a microemulsion, containing 1.4% of the reaction product prepared in Example 21, in which a piece of polyester cotton (65/35) was treated by padding. The piece was heated to 110°C for 90 seconds, followed by heating at 180°C for 2 minutes and 150°C for 5 minutes respectively for Examples 21 and 22 after treatment. The pieces had picked up 1% and 0.5% by weight of the reaction product respectively.

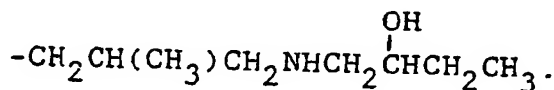
Example 23

20 1 mole of $(\text{CH}_3\text{O})_2\text{Si}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{NH}(\text{CH}_2)_2\text{NH}_2$ and methanol were added to a reaction vessel. 1.1 mole of 1,2 butyleneoxide were added through a dropping funnel and the mixture was heated under a nitrogen blanket to 50°C which was maintained for 1 hour. The product was stripped under reduced pressure on a rotary evaporator. 1 mole of the product was mixed with 3 moles of water and heated to 110°C to allow condensation of the silanes. After purification hexamethyldisiloxane and cyclic dimethylsiloxane were added together with an alkaline catalyst. The mixture was heated for 5 hours to 140°C and then neutralised. The filtered reaction product had the formula



wherein R'

denotes



40 The reaction product was applied to a piece of polyester cotton according to the method described for Example 22.

Comparative Examples 1 - 10

45 A bath was prepared with a 2.77% solution in perchloro ethylene of the amino containing polydiorganosiloxane used in Examples 11 to 15 on its own, in which a piece of polyester cotton (65/35) was treated by padding. The piece picked up 0.5% by weight of the siloxane. (Comparative Example 1).

50 As in Comparative Example 1, but using a mixture of 1 molar part of the polydiorganosiloxane of Comparative Example 1 with 2 molar parts of propylene oxide, but not reacted. (Comparative Example 2).

Comparative Example 3 was a piece of untreated polyester cotton (blank) as used in Examples 11 to 15.

55 A bath was prepared with a 2.77% solution in perchloro ethylene of the amino containing polydiorganosiloxane used in Examples 16 to 20 on its own, in which a piece of polyester cotton (65/35) was treated by padding. The piece picked up 0.5% by weight of the siloxane. (Comparative Example 4).

Comparative Example 5 was a piece of untreated polyester cotton (blank) as used in Examples 16 to 20.

Comparative Example 6 was a microemulsion of a mixture of the two reactants of Example 21, in the

same proportions and with the same concentration, in which a piece of polyester cotton (65/35) was treated by padding. The piece picked up 1% by weight of the siloxane.

Comparative Example 7 was a microemulsion of the amino containing polydiorganosiloxane of Example 21 on its own in the same concentration, in which a piece of polyester cotton (65/35) was treated by padding. The piece picked up 1% by weight of the siloxane.

Comparative Example 8 was a piece of untreated polyester cotton (blank) as used in Example 21.

Comparative Example 9 was a piece of untreated polyester cotton (blank) as used in Examples 22 and 23.

Comparative Example 10 was a microemulsion of the amino containing polydiorganosiloxane of Example 22 on its own in the same concentration, in which a piece of polyester cotton (65/35) was treated by padding. The piece picked up 0.5% by weight of the siloxane.

All comparative treated pieces of polyester-cotton were heated to 110° C for 1 minute followed by 2 minutes at 180° C for Comparative Examples 1 to 8 and 5 minutes at 150° C for Comparative Examples 9 and 10. The treated pieces of polyester cotton of Examples 1 to 23 were compared for softness and yellowing effect. It was found that the increase in molecular weight of the siloxane polymer used gave also an increase in the softness of the treated material. Within each series of similar molecules the best softness was obtained by those materials where n had a value of 0, 1 or 3.

The whiteness index of Examples 16 to 20 were measured using a Hunterlab Optical sensor, Model D25M and were compared with Comparative Examples 4 and 5. The following results were obtained.

Example	Whiteness Index
16	73.2
17	71.6
18	74.8
19	74.0
20	73.3
Comparative 4	62.5
Comparative 5	75.7

The whiteness index of Example 11 was measured using a Hunterlab Optical sensor, Model D25M and compared with Comparative Examples 1, 2 and 3. The following results were obtained:

Example	Whiteness Index
11	68.8
Comparative 1	60.4
Comparative 2	59.7
Comparative 3	69.6

The whiteness index of Example 21 was measured using a Hunterlab Optical sensor, Model D25M and compared with Comparative Examples 6, 7 and 8. The following results were obtained:

Example	Whiteness Index
21	72.6
Comparative 6	65.1
Comparative 7	58.0
Comparative 8	76.4

The whiteness index of Examples 22 and 23 was measured using a Hunterlab Optical sensor, Model

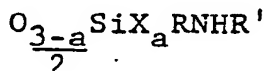
D25M and compared with Comparative Examples 9 and 10. The following results were obtained:

Example	Whiteness Index
22	80.8
23	78.3
Comparative 9	81.7
Comparative 10	74.8

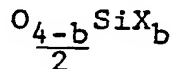
It can be seen from the results that the method according to the invention yields treated materials which have very little yellowing in comparison with materials treated according to the prior art, and have a whiteness index which is very close to that of the untreated material.

Claims

1. A method of treating fibrous materials which comprises the application to the fibrous materials of a composition comprising an amine containing organosilicon compound, characterised in that the sole amine containing organosilicon compound in the composition is the reaction product of an organopolysiloxane having at least one unit of the general formula



and at least one unit of the general formula

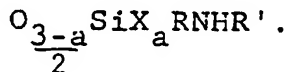


with one or more monoepoxides wherein X denotes a monovalent hydrocarbon group having up to 8 carbon atoms, R denotes a divalent alkylene group, R' denotes a hydrogen atom or a group of the formula RZ wherein Z is NHX, NH₂, NHRNH₂ or NHRNHX, a has a value of 1 or 2 and b has a value of 2 or 3.

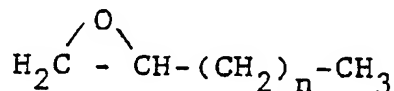
2. A method according to Claim 1 characterised in that the organopolysiloxane is a substantially linear polydiorganosiloxane wherein at least 80% of all X groups are methyl groups.

3. A method according to either Claim 1 or Claim 2 characterised in that the organopolysiloxane comprises from 100 to 500 siloxane units.

4. A method according to any one of the preceding claims characterised in that from 1 to 10 mole% of all siloxane units of the organopolysiloxane are units of the formula



5. A method according to any one of the preceding claims characterised in that the monoepoxide has the general formula



wherein n has a value of from 0 to 8.

6. A method according to any one of the preceding claims characterised in that the majority of amine groups in the reaction product are tertiary amine groups, there being no more than 10% primary amine

groups present in said reaction product.

7. A method according to any one of the preceding claims characterised in that the reaction product does not contain any primary or secondary amine groups.

8. A method according to any one of the preceding claims characterised in that the composition is in the form of an emulsion.

9. A method according to any one of the preceding claims characterised in that the composition comprises no other amine containing compounds than the reaction product.

10. Textiles incorporating fibres characterised in that the fibres have been treated by a method according to any one of the preceding claims.



2 1 1

—

—

1

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 399 706 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90305117.5

(51) Int. Cl.⁵: D06M 15/643

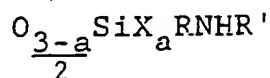
(22) Date of filing: 11.05.90

(30) Priority: 24.05.89 GB 8911970

(43) Date of publication of application:
28.11.90 Bulletin 90/48(84) Designated Contracting States:
BE DE ES FR GB IT NL(88) Date of deferred publication of the search report:
20.03.91 Bulletin 91/12(71) Applicant: Dow Corning Limited
Inveresk House 1 Aldywch
London WC2R 0HF(GB)(72) Inventor: Cray, Stephen Edward
10 Doniford Close Sully
South Glamorgan Wales(GB)
Inventor: Renault, Franck André Daniel
Schransdreef 49
B-1900 Overijse(BE)(74) Representative: Vandamme, Luc Johan Roger
et al
Dow Corning Limited Cardiff Road
Barry South Glamorgan CF6 7YL Wales(GB)

(54) Method of treating fibrous materials.

(57) A method of treating fibrous materials comprises applying a composition comprising as sole amine containing organosilicon compound the reaction product of an organopolysiloxane having



groups with one or more monoepoxides. X denotes a monovalent C₁₋₈ hydrocarbon group, R is an alkylene group, R' is H or a group of the formula RZ, Z being NHX, NH₂, NHRNH₂ or NHRNHX. No more than 10% of all amine groups may be primary amine groups. The composition is preferably applied as an emulsion. Fibres thus treated are soft and show less yellowing than the prior art.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 90305117.5

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D, X	<u>US - A - 4 757 121</u> (TANAKA et al.) * Claims; column 6, lines 26-28 * -----	1, 8, 10	D 06 M 15/643
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			D 06 M
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 11-12-1990	Examiner BECK
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	